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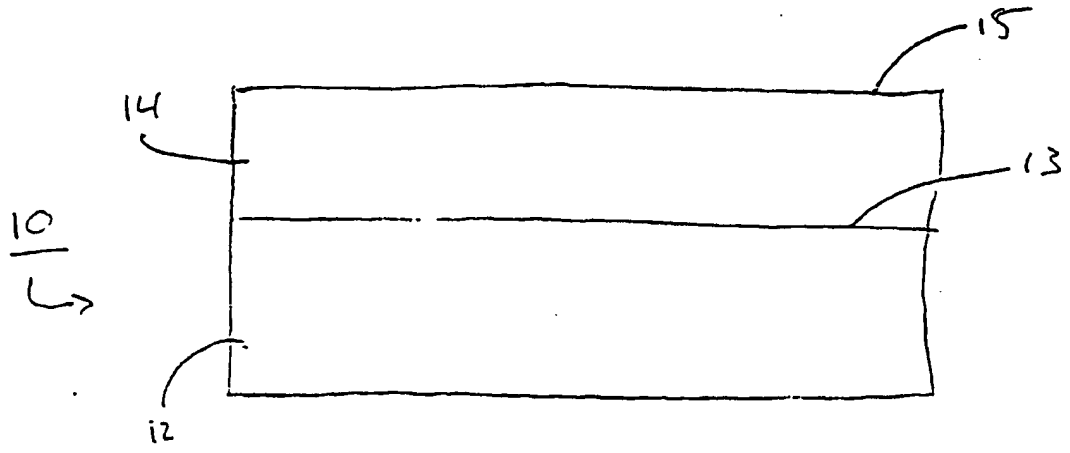
(54) Title: METHODS OF MAKING A SUPERCONDUCTOR



(57) Abstract: The invention relates to methods of making a superconductor. The compositions can be used in methods using relatively few temperature ramps, varying pressures of water vapor, and/or isothermal treatment steps. The methods and compositions can be used to form superconductor material intermediates that have relatively few cracks and/or blisters.

WO 01/08231 A2

Methods of Making A Superconductor

Background of the Invention

The invention relates to methods of making a superconductor.

Multi-layer articles can be used in a variety of applications. For example, superconductors, including oxide superconductors, can be formed of multi-layer articles. Typically, such superconductors include a layer of superconductor material and a layer, commonly referred to as a substrate, that can enhance the mechanical strength of the multi-layer article.

Generally, in addition to enhancing the strength of the multi-layer superconductor, the substrate should exhibit certain other properties. For example, the substrate should have a low Curie temperature so that the substrate is not ferromagnetic at the superconductor's application temperature. Furthermore, chemical species within the substrate should not be able to diffuse into the layer of superconductor material, and the coefficient of thermal expansion of the substrate should be about the same as the superconductor material. Moreover, if the substrate is used for an oxide superconductor, the substrate material should be relatively resistant to oxidation.

For some materials, such as yttrium-barium-copper-oxide (YBCO), the ability of the material to provide high transport current in its superconducting state depends upon the crystallographic orientation of the material. For example, such a material can exhibit a relatively high critical current density (Jc) when the surface of the material is biaxially textured.

As used herein, "biaxially textured" refers to a surface for which the crystal grains are in close alignment with a direction in the plane of the surface. One type of biaxially textured surface is a cube textured surface, in which the crystal grains are also

in close alignment with a direction perpendicular to the surface. Examples of cube textured surfaces include the (100)[001] and (100)[011] surfaces, and an example of a biaxially textured surface is the (113)[211] surface.

For certain multi-layer superconductors, the layer of superconductor material is an epitaxial layer. As used herein, "epitaxial layer" refers to a layer of material whose crystallographic orientation is directly related to the crystallographic orientation of the surface of a layer of material onto which the epitaxial layer is deposited. For example, for a multi-layer superconductor having an epitaxial layer of superconductor material deposited onto a substrate, the crystallographic orientation of the layer of superconductor material is directly related to the crystallographic orientation of the substrate. Thus, in addition to the above-discussed properties of a substrate, it can be also desirable for a substrate to have a biaxially textured surface or a cube textured surface.

Some substrates do not readily exhibit all the above-noted features, so one or more intermediate layers, commonly referred to as buffer layers, can be disposed between the substrate and the superconductor layer. The buffer layer(s) can be more resistant to oxidation than the substrate, and reduce the diffusion of chemical species between the substrate and the superconductor layer. Moreover, the buffer layer(s) can have a coefficient of thermal expansion that is well matched with the superconductor material.

Typically, a buffer layer is an epitaxial layer, so its crystallographic orientation is directly related to the crystallographic orientation of the surface onto which the buffer layer is deposited. For example, in a multi-layer superconductor having a substrate, an epitaxial buffer layer and an epitaxial layer of superconductor material, the crystallographic orientation of the surface of the buffer layer is directly related to the

crystallographic orientation of the surface of the substrate, and the crystallographic orientation of the layer of superconductor material is directly related to the crystallographic orientation of the surface of the buffer layer. Therefore, the superconducting properties exhibited by a multi-layer superconductor having a buffer layer can depend upon the crystallographic orientation of the buffer layer surface.

Summary of the Invention

The invention relates to methods of making a superconductor.

In one embodiment, the invention features a method that includes treating a coating using less than three temperature ramps (e.g., two temperature ramps) to form a metal oxyfluoride intermediate of a rare earth metal-second metal-first metal-oxide superconductor.

The method can include heating to a first temperature of from about 215°C to about 225°C (e.g., about 220°C) and maintaining the first temperature for at least about one hour in a first gas environment having a first water vapor pressure (e.g., from about 5 Torr to about 40 Torr). The gas environment can then be switched to a second gas environment having a second water vapor pressure different than the first water vapor pressure. The first temperature can be maintained for at least about one hour in the second gas environment. The second water vapor pressure can be less than the first water vapor pressure (e.g., less than about one Torr).

The method can further include heating to a second temperature (e.g., about 400°C) different than the first temperature and maintaining the second temperature for a time period sufficient to form the metal oxyfluoride intermediate. Heating to the second temperature can be performed in the second gas environment.

The method can further include heating to a third temperature (e.g., at least about 700°C) to form the rare earth-second metal-first metal-oxide superconductor.

In another aspect, the invention features a method that includes heating a coating to a first temperature and maintaining the first temperature for a first time period. The first temperature is greater than room temperature (e.g., about 50°C), and the first period of time is at least about one minute. The method also includes heating to a second temperature (e.g., about 400°C) greater than the first temperature to form a metal oxyfluoride intermediate of a rare earth-second metal-first metal-oxide superconductor.

In a further aspect, the invention features a method that includes heating a coating to a first temperature, and maintaining the first temperature for a first period of time (e.g., at least about one hour) in a first gas environment having a first water vapor pressure. The first temperature is greater than room temperature, and the first period of time is at least about one minute. The method further includes maintaining the first temperature for a second period of time (e.g., at least about one hour) in a second gas environment having a second water vapor pressure different than the first water vapor pressure. The second time period is at least about one minute. The method also includes heating to a second temperature greater than the first temperature to form a metal oxyfluoride intermediate of a rare earth-second metal-first metal-oxide superconductor. The first water vapor pressure (e.g., about 5 Torr to about 40 Torr) can be greater than the second water vapor pressure (e.g., less than about one Torr).

The methods can further include, prior to treating the coating, disposing the coating on a surface of a first layer of material.

The intermediate can have a surface adjacent the surface of the first layer of material and a plurality of volume elements so that defects contained within the intermediate comprise less than about 20 percent of any volume element of the intermediate defined by a projection of one square centimeter of the surface of the

intermediate, and the intermediate is free of any defect having a maximum dimension of greater than about 200 microns.

As used herein, a "defect" refers to a crack or a blister, such as a crack or a blister that is detectable by visual (or optical) inspection.

A volume element of a layer of material defined by the projection of a given area of a surface of the layer of material corresponds to the volume of the layer of material whose edges are perpendicular to the given area of the surface of the layer of material.

The first metal can be copper, and the second metal can be barium, strontium or calcium (e.g., barium). The rare earth metal can be yttrium. The rare earth metal-second metal-first metal-oxide can be yttrium-barium-copper-oxide.

The intermediate can have a thickness of at least about 0.5 micron.

The intermediate can be, for example, partially or completely formed of one or more metal oxyfluoride compounds.

One potential advantage of the invention is that it can provide methods of making high quality superconductor layers or layers of superconductor intermediate (e.g., metal oxyfluoride intermediate) using relatively few temperature ramps. For example, the methods and compositions can be used to prepare a superconductor intermediate using fewer than three temperature ramps (e.g., two temperature ramps). The resulting superconductor layer can have a relatively low defect density and/or a relatively high critical current density.

Another potential advantage of the invention is that it can provide methods of making high quality superconductor layers or layers of superconductor intermediate (e.g., metal oxyfluoride intermediate) that include one or more steps where the temperature is maintained substantially constant (e.g., constant within about 10°C,

within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., at least about one minute, at least about five minutes, at least about 30 minutes, at least about one hour, at least about two hours, at least about four hours). The resulting superconductor layer can have a relatively low defect density and/or a relatively high critical current density.

The methods of the invention can be particularly advantageous when used to prepare a superconductor (e.g., an oxide superconductor), or an intermediate of such a superconductor, in the form of an object having a relatively large surface area, such as a wafer or a tape.

In certain embodiments, the methods and compositions of the invention can be particularly advantageous when used to prepare relatively thick oxide superconductor layers (e.g., layers having a thickness of greater than about 0.5 micron, such as greater than about 0.8 micron or greater than about one micron).

In some embodiments, the superconductor material is preferably formed of YBCO (e.g., $YBa_2Cu_3O_{7-x}$).

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice of the invention, suitable methods and materials are described below. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the description of the preferred embodiments, the figures and the claims.

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of one embodiment of a multi-layer article;

Fig. 2 is a cross-sectional view of another embodiment of a multi-layer article; and

Fig. 3 is a cross-sectional view of a further embodiment of a multi-layer article.

Description of the Preferred Embodiments

The invention relates to methods of making a superconductor. The methods generally include heating a composition (e.g., a precursor solution) to form a metal oxyfluoride intermediate, and heating the metal oxyfluoride intermediate to form the superconductor (e.g., an oxide superconductor).

In certain embodiments, the precursor composition has a relatively small amount of free acid. In aqueous solutions, this can correspond to a precursor composition with a relatively neutral pH (e.g., neither strongly acidic nor strongly basic). The precursor composition can be used to prepare multi-layer superconductors using a wide variety of materials which can be used as the underlying layer on which the superconductor layer is formed.

The total free acid concentration of the precursor composition can be less than about $1x10^{-3}$ molar (e.g., less than about $1x10^{-5}$ molar or about $1x10^{-7}$ molar). Examples of free acids that can be contained in a precursor composition include trifluoroacetic acid, acetic acid, nitric acid, sulfuric acid, acids of iodides, acids of bromides and acids of sulfates.

When the precursor composition contains water, the precursor composition can have a pH of at least about 3 (e.g., at least about 5 or about 7).

In some embodiments, the precursor composition can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, less than about 25 volume percent water).

In embodiments in which the precursor composition contains trifluoroacetic acid and an alkaline earth metal (e.g., barium), the total amount of trifluoroacetic acid can be selected so that the mole ratio of fluorine contained in the precursor composition (e.g., in the form of trifluoroacetate) to the alkaline earth metal (e.g., barium ions) contained in the precursor composition is at least about 2:1 (e.g., from about 2:1 to about 18.5:1, or from about 2:1 to about 10:1).

In these embodiments, the precursor compositions can be prepared by combining soluble compounds of a first metal (e.g., copper), a second metal (e.g., an alkaline earth metal), and a rare earth metal with one or more desired solvents and optionally water. As used herein, "soluble compounds" of the first, second and rare earth metals refer to compounds of these metals that are capable of dissolving in the solvent(s) contained in the precursor compositions. Such compounds include, for example, salts (e.g., nitrates, acetates, alkoxides, iodides, sulfates and trifluoroacetates), oxides and hydroxides of these metals.

In alternate embodiments, a precursor solution is formed of an organic solution containing metal trifluoroacetates prepared from powders of $BaCO_3$, $YCO_3 \cdot 3H_2O$ and $Cu(OH)_2CO_3$ combined and reacted using methods known to those skilled in the art. For example, the powders can be combined in a 2:1:3 ratio with between 20-30% (5.5-6.0 M) excess trifluoroacetic acid in methyl alcohol and then refluxed (e.g., for approximately four to ten hours) to produce a solution substantially 0.94 M based on copper content.

The methods of the invention can be used to prepare the superconductor intermediate (e.g., metal oxyfluoride) from the initial composition using relatively few temperature ramps (e.g., fewer than three temperature ramps, such as two temperature ramps).

The methods of the invention can be used to prepare the metal oxyfluoride intermediate while maintaining the temperature substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours, more than about four hours) after a first temperature ramp to a temperature greater than about room temperature (e.g., to a temperature of at least about 50°C, at least about 100°C, at least about 200°C, at least about 215°C, from about 215°C to about 225°C, about 220°C).

The methods of the invention can be used to prepare the metal oxyfluoride intermediate using more than one gas environment while maintaining the temperature substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours, more than about four hours). For example, the water vapor pressure can be varied (e.g., from a relatively high water vapor pressure to a relatively low water vapor pressure) while the temperature is held substantially constant for a relatively long period of time. In certain embodiments, while maintaining the temperature substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C), the water vapor pressure can be at least about 5 Torr (e.g., from about 5 Torr to about 40 Torr, from about 15 Torr to

about 38 Torr, about 32 Torr, or about 17 Torr) for a period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours), then reduced to less than about one Torr (e.g., less than about 0.1 Torr, less than about 10 milliTorr, about five milliTorr) for a period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours).

In preferred embodiments, the metal oxyfluoride intermediate has a relatively low defect density. Preferably, defects contained within the layer of the intermediate make up less than about 20 percent (e.g., less than about 10 percent, or less than about five percent) of any volume element of the layer of the intermediate defined by the projection of one square centimeter of the surface of the layer of the intermediate.

Preferably, the metal oxyfluoride intermediate is free of any defect having a maximum dimension of greater than about 200 microns, more preferably the intermediate is free of any defect having a maximum dimension of greater than about 100 microns, and most preferably the intermediate is free of any defect having a maximum dimension of greater than about 50 microns.

The methods of disposing the composition on the underlying layer include spin coating, dip coating, web coating and other techniques known in the art.

In some embodiments in which spin coating is used, the composition is disposed on the underlying layer and the spin rate is ramped from about zero revolutions per minute (RPM) to from about 500 RPM to about 3,000 RPM in about 0.5 second. This spin rate is held for about five seconds, and the spin rate is then ramped to from about 1,000 RPM to about 5,000 RPM in about 0.5 second. This spin rate is held for about 60 seconds, and the spin rate is then decreased to about zero RPM. As known to those skilled in the art, other spin coating conditions can also be used.

The composition is then heated. Generally, this step is performed to remove excess solvent (e.g., water and methanol) from the composition and to decompose the metalorganic molecules to one or more oxyfluoride intermediate of the desired superconductor material. The final temperature used during this step is generally selected so that the composition (e.g., precursor solution) is converted to a brown film.

Typically, the initial temperature in this step is about room temperature, and the final temperature is from about 215°C to about 225°C (e.g., about 220°C). Preferably, this step is performed using a temperature ramp of 10°C per minute or less (e.g., 8°C per minute or less, 5°C per minute or less). During this step, the partial pressure of water vapor in the nominal gas environment is preferably maintained at from about 5 Torr to about 40 Torr (e.g., from about 17 Torr to about 38 Torr, about 32 Torr, or about 17 Torr). The partial pressure of oxygen in the nominal gas environment can be maintained at from about 0.1 Torr to about 760 Torr.

The temperature and nominal gas environment are then held substantially constant for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours).

After this time period, the gas environment is changed to a relatively dry gas environment (e.g., less than about one Torr water vapor, less than about 0.1 Torr water vapor, less than about 10 milliTorr water vapor, five milliTorr water vapor) while maintaining the temperature substantially constant. The temperature and nominal gas environment are then held substantially constant for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about one hour, more than about two hours).

After this time period, the nominal gas environment is maintained substantially constant and heating is continued to a temperature sufficient to form the metal oxyfluoride intermediate (e.g., about 400°C). This step is preferably performed using a temperature ramp of 10°C per minute or less (e.g., 8°C per minute or less, 5°C per minute or less).

The metal oxyfluoride intermediate can then be heated to form the desired superconductor layer. Typically, this step is performed by heating to a temperature of from about 700°C to about 825°C. During this step, the nominal gas environment typically can contain from about 0.1 Torr to about 50 Torr oxygen and from about 0.1 Torr to about 150 Torr (e.g., about 12 Torr) of water vapor with the balance being nitrogen and/or argon.

In alternate embodiments, the metal oxyfluoride intermediate is heated for about one hour to a temperature of less than about 860°C (e.g., less than about 810°C) in a moist reducing nitrogen-oxygen gas mixture (e.g., having a composition including from about 0.5% to about 5% oxygen). The coating can be further heated to a temperature of from about 860°C to about 950°C for from about five to about 25 minutes. The coating is subsequently heated to a temperature of from about 400°C to about 500°C for at least about eight hours at in dry oxygen. The coating can then be cooled to room temperature in static dry oxygen, such as described in U.S. Patent No. 5,231,074.

In still other embodiments, the metal oxyfluoride is converted into an oxide superconductor in a processing gas having a moisture content of less than 100% relative humidity (e.g., less than about 95% relative humidity, less than about 50% relative humidity, or less than about 3% relative humidity) at 25°C to form some oxide superconductor, then completing the conversion using a processing gas having a higher moisture content (e.g., from about 95% relative humidity to about 100% relative

humidity at 25°C). The temperature for converting the metal oxyfluoride can be in the range of from about 700°C to about 900°C (e.g., from about 700°C to about 835°C). The processing gas preferably contains from about 1 volume percent oxygen gas to about 10 volume percent oxygen gas.

In particular embodiments, when preparing the superconductor material from the precursor solution, methods can be employed to minimize the formation of undesirable a-axis oriented oxide layer grains, by inhibiting the formation of the oxide layer until the required reaction conditions are attained.

Conventional processes developed for decomposition and reaction of fluoride-containing precursors use a constant, and low, non-turbulent flow of process gas that is introduced into the decomposition furnace in an orientation that is parallel to the film surface, resulting in a stable boundary layer at the film/gas interface. In the apparatus types typically used for oxide layer precursor decomposition and reaction, the diffusion of gaseous reactants and products through this gas/film boundary layer appears to control the overall reaction rates. In thin, small area films (for example, less than about 0.4 microns thick and less than about a square centimeter), the diffusion of H_2O into the film and the diffusion of HF out of the film occur at rates such that the formation of the $YBa_2Cu_3O_{7-x}$ phase does not begin at any significant rate until the sample reaches the processing temperature. However, as the film thickness or area increases, the rates of gaseous diffusion into and out of the film decrease, all other parameters being equal. This results in longer reaction times and/or incomplete formation of the $YBa_2Cu_3O_{7-x}$ phase, resulting in reduced crystallographic texture, lower density, and reduced critical current density. Thus, the overall rate of $YBa_2Cu_3O_{7-x}$ phase formation is determined, to a significant extent, by the diffusion of gases through the boundary layer at the film surface.

One approach to eliminating these boundary layers is to produce a turbulent flow at the film surface. Under such conditions, the local gas composition at the interface is maintained essentially the same as in the bulk gas (that is, the pH_2O is constant, and the pHF is approximately zero). Thus, the concentration of the gaseous products/reactants in the film is not controlled by the diffusion through the gas/film surface boundary layer condition, but rather by diffusion through the film. In order to minimize the nucleation of a-axis $YBa_2Cu_3O_{7-x}$ oriented grains on a substrate surface, the formation of the $YBa_2Cu_3O_{7-x}$ phase is inhibited until desired process conditions are reached. For example, the formation of the $YBa_2Cu_3O_{7-x}$ phase can be inhibited until desired process temperature is reached.

In one embodiment, a combination of: 1) low (non-turbulent) process gas flow, so that a stable boundary layer is established at the film/gas interface, during the ramp to temperature, and 2) high (turbulent) process gas flow, so that the boundary layer is disrupted at the film/gas interface, is employed. For example, in a three inch tube furnace, the flow can be from about 0.5 to about 2.0 L/min during the temperature ramp from ambient temperature to the desired process temperature. Thereafter, the flow can be increased to a value of from about 4 to about 15 L/min during the time at which the film is being processed. Thus, the rate of formation of $YBa_2Cu_3O_{7-x}$ and epitaxial texture formation can be increased at high temperature, while minimizing the amount of unwanted a-axis nucleation and growth at low temperature during ramp up. According to these processes, a-axis nucleated grains are desirably present in an amount of less than about 1%, as determined by scanning electron microscopy.

Fig. 1 shows a multi-layer superconductor article 10 according to one embodiment of the invention and prepared using the above-described methods and

compositions. Article 10 includes a substrate layer 12 with a surface 13 and a superconductor material layer 14 with a surface 15. Layer 14 is disposed on surface 13.

Layer 12 can be formed of any material capable of supporting layer 14. In embodiments in which article 10 is a multi-layer superconductor, layer 12 can be formed of a substrate material. Examples of substrate materials that can be used as layer 12 include for example, metals and/or alloys, such as nickel, silver, copper, zinc, aluminum, iron, chromium, vanadium, palladium, molybdenum and/or their alloys. In some embodiments, article 10 can be in the form of an object having a relatively large surface area (e.g., a wafer or a tape), and layer 12 can be formed of a relatively flexible material.

Surface 13 of layer 12 can also be prepared using vacuum processes, such as ion beam assisted deposition, inclined substrate deposition and other vacuum techniques known in the art to form a biaxially textured surface on, for example, a randomly oriented polycrystalline surface.

In some embodiments, a buffer layer can be formed using ion beam assisted deposition (IBAD). In this technique, a buffer layer material is evaporated using, for example, electron beam evaporation, sputtering deposition, or pulsed laser deposition while an ion beam (e.g., an argon ion beam) is directed at a smooth amorphous surface of a substrate onto which the evaporated buffer layer material is deposited.

For example, the buffer layer can be formed by ion beam assisted deposition by evaporating a buffer layer material having a rock-salt like structure (e.g., a material having a rock salt structure, such as an oxide, including MgO, or a nitride) onto a smooth, amorphous surface (e.g., a surface having a root mean square roughness of less than about 100 Angstroms) of a substrate so that the buffer layer material has a surface with substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

The conditions used during deposition of the buffer layer material can include, for example, a substrate temperature of from about 0°C to about 400°C (e.g., from about room temperature to about 400°C), a deposition rate of from about 1.0 Angstrom per second to about 4.4 Angstroms per second, an ion energy of from about 200 eV to about 1200 eV, and/or an ion flux of from about 110 microamperes per square centimeter to about 120 microamperes per square centimeter.

In some embodiments, when using IBAD, the substrate is formed of a material having a polycrystalline, non-amorphous base structure (e.g., a metal alloy, such as a nickel alloy) with a smooth amorphous surface formed of a different material (e.g., Si_3N_4).

In certain embodiments, a plurality of buffer layers can be deposited by epitaxial growth on an original IBAD surface. Each buffer layer can have substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

In other embodiments, the substrate can be formed of alloys having one or more surfaces that are biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[001] or (100)[011]). The alloys can have a relatively low Curie temperature (e.g., at most about 80K, at most about 40K, or at most about 20K).

In some of these embodiments, the substrate is a binary alloy that contains two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. For example, a binary alloy can be formed of nickel and chromium (e.g., nickel and at most 20 atomic percent chromium, nickel and from about five to about 18 atomic percent chromium, or nickel and from about 10 to about 15 atomic percent chromium). As another example, a binary alloy can be formed of nickel and copper (e.g., copper and from about five to about 45 atomic percent nickel, copper and from about 10 to about 40 atomic percent nickel, or copper and from

about 25 to about 35 atomic percent nickel). A binary alloy can further include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

In certain of these embodiments, the substrate contains more than two metals (e.g., a ternary alloy or a quarternary alloy). In these embodiments the alloy can contain one or more oxide formers (e.g., Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb and/or La, with Al being the preferred oxide former), as well as two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. The alloys can contain at least about 0.5 atomic percent oxide former (e.g., at least about one atomic percent oxide former, or at least about two atomic percent oxide former) and at most about 25 atomic percent oxide former (e.g., at most about 10 atomic percent oxide former, or at most about four atomic percent oxide former). For example, the alloy can include an oxide former (e.g., at least about 0.5 aluminum), from about 25 atomic percent to about 55 atomic percent nickel (e.g., from about 35 atomic percent to about 55 atomic percent nickel, or from about 40 atomic percent to about 55 atomic percent nickel) with the balance being copper. As another example, the alloy can include an oxide former (e.g., at least about 0.5 atomic aluminum), from about five atomic percent to about 20 atomic percent chromium (e.g., from about 10 atomic percent to about 18 atomic percent chromium, or from about 10 atomic percent to about 15 atomic percent chromium) with the balance being nickel. The alloys can include relatively small amounts of additional metals (e.g., less than about 0.1 atomic percent of additional metals, less than about 0.01 atomic percent of additional metals, or less than about 0.005 atomic percent of additional metals).

A substrate formed of an alloy can be produced by, for example, combining the constituents in powder form, melting and cooling or, for example, by diffusing the powder constituents together in solid state. The alloy can then be formed by deformation texturing (e.g, annealing and rolling, swaging, extrusion and/or drawing) to form a textured surface (e.g., biaxially textured or cube textured). Alternatively, the alloy constituents can be stacked in a jelly roll configuration, and then deformation textured. In some embodiments, a material with a relatively low coefficient of thermal expansion (e.g, Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni_3Al, or mixtures thereof) can be formed into a rod and embedded into the alloy prior to deformation texturing.

In some embodiments, stable oxide formation can be mitigated until a first epitaxial (for example, buffer) layer is formed on the biaxially textured alloy surface, using an intermediate layer disposed on the surface of the substrate. Intermediate layers suitable for use in the present invention include those epitaxial metal or alloy layers that do not form surface oxides when exposed to conditions as established by P_{O2} and temperature required for the initial growth of epitaxial buffer layer films. In addition, the buffer layer acts as a barrier to prevent substrate element(s) from migrating to the surface of the intermediate layer and forming oxides during the initial growth of the epitaxial layer. Absent such an intermediate layer, one or more elements in the substrate would be expected to form thermodynamically stable oxide(s) at the substrate surface which could significantly impede the deposition of epitaxial layers due to, for example, lack of texture in this oxide layer.

In some of these embodiments, the intermediate layer is transient in nature. "Transient," as used herein, refers to an intermediate layer that is wholly or partly incorporated into or with the biaxially textured substrate following the initial nucleation

and growth of the epitaxial film. Even under these circumstances, the intermediate layer and biaxially textured substrate remain distinct until the epitaxial nature of the deposited film has been established. The use of transient intermediate layers may be preferred when the intermediate layer possesses some undesirable property, for example, the intermediate layer is magnetic, such as nickel.

Exemplary intermediate metal layers include nickel, gold, silver, palladium, and alloys thereof. Additional metals or alloys may include alloys of nickel and/or copper. Epitaxial films or layers deposited on an intermediate layer can include metal oxides, chalcogenides, halides, and nitrides. In preferred embodiments, the intermediate metal layer does not oxidize under epitaxial film deposition conditions.

Care should be taken that the deposited intermediate layer is not completely incorporated into or does not completely diffuse into the substrate before nucleation and growth of the initial buffer layer structure causes the epitaxial layer to be established. This means that after selecting the metal (or alloy) for proper attributes such as diffusion constant in the substrate alloy, thermodynamic stability against oxidation under practical epitaxial buffer layer growth conditions and lattice matching with the epitaxial layer, the thickness of the deposited metal layer has to be adapted to the epitaxial layer deposition conditions, in particular to temperature.

Deposition of the intermediate metal layer can be done in a vacuum process such as evaporation or sputtering, or by electro-chemical means such as electroplating (with or without electrodes). These deposited intermediate metal layers may or may not be epitaxial after deposition (depending on substrate temperature during deposition), but epitaxial orientation can subsequently be obtained during a post-deposition heat treatment.

Preferably, surface 13 of layer 12 has a relatively well defined crystallographic orientation. For example, surface 13 can be a biaxially textured surface (e.g., a (113)[211] surface) or a cube textured surface (e.g., a (100)[011] surface or a (100)[001] surface). Preferably, the peaks in an X-ray diffraction pole figure of surface 13 have a FWHM of less than about 20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°).

In certain embodiments, solution coating processes can be used for deposition of one or a combination of any of the oxide layers on textured substrates; however, they can be particularly applicable for deposition of the initial (seed) layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of the substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent oxide layers. In order to meet these requirements, the seed layer should grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

The formation of oxide buffer layers can be carried out so as to promote wetting of an underlying substrate layer. Additionally, in particular embodiments, the formation of metal oxide layers can be carried out using metal alkoxide precursors (for example, "sol gel" precursors), in which the level of carbon contamination can be greatly reduced over other known processes using metal alkoxide precursors.

If the substrate underlying an oxide layer is insufficiently covered by a precursor solution used to make the oxide layer, then the first oxide layer may not provide the desired protection of the substrate from oxidation during deposition of the

subsquent oxide layers when carried out in an oxidizing atmosphere relative to the substrate and may not provide a complete template for the epitaxial growth of subsquent layers. By heating a sol gel precursor film, and thereby allowing the precursor to flow into the substrate grain boundary areas, complete coverage can result. The heating can be relatively low temperature, for example, from about 80°C to about 320°C, for example, from about 100°C to about 300°C, or from about 100°C to about 200°C. Such temperatures can be maintained from about 1 to about 60 minutes, for example, from about 2 to about 45 minutes, or from about 15 to about 45 minutes. The heating step can also be carried out using higher temperatures for a shorter time, for example, a film can be processed within two minutes at a temperature of 300°C.

This heating step can be carried out after, or concurrently with, the drying of excess solvent from the sol gel precursor film. It must be carried out prior to decomposition of the precursor film, however.

The carbon contamination accompanying conventional oxide film preparation in a reducing environment (e.g., 4%H_2-Ar) is believed to be the result of an incomplete removal of the organic components of the precursor film. The presence of carbon-containing contaminants C_xH_y and $C_aH_bO_c$ in or near the oxide layer can be detrimental, since they can alter the epitaxial deposition of subsequent oxide layers. Additionally, it is likely that the trapped carbon-containing contaminants buried in the film can be oxidized during the processing steps for subsequent oxide layers, which can utilize oxidizing atmospheres. The oxidation of the carbon-containing contaminants can result in CO_2 formation, and the subsequent blistering of the film, and possible delamination of the film, or other defects in the composite structure. Thus, it is undesirable to allow carbon-containing contaminants arising from metal alkoxide decomposition to become oxidized only after the oxide layer is formed. Preferably, the

carbon-containing contaminants are oxidized (and hence removed from the film structure as CO_2) as the decomposition occurs. Also the presence of carbon-containing species on or near film surfaces can inhibit the epitaxial growth of subsequent oxide layers.

According to particular embodiments, after coating a metal substrate or buffer layer, the precursor solution can be air dried, and then heated in an initial decomposition step. Alternatively, the precursor solution can be directly heated in an initial decomposition step, under an atmosphere that is reducing relative to the metal substrate. Once the oxide layer initially nucleates on the metal substrate in the desired epitaxial orientation, the oxygen level of the process gas is increased, for example, by adding water vapor or oxygen. The nucleation step requires from about 5 minutes to about 30 minutes to take place under typical conditions.

Layer 14 can be prepared using the above-described methods. Preferably, layer 14 is formed of a rare earth metal-barium-copper-oxide (REBCO), such as YBCO (e.g., $YBa_2Cu_3O_{7-x}$). Preferably, layer 14 has a thickness of from about 0.5 micron to about 10 microns.

In preferred embodiments, layer 14 has a relatively low defect density. Preferably, defects contained within layer 14 make up less than about 20 percent (e.g., less than about 10 percent, or less than about five percent) of any volume element of layer 14 defined by the projection of one square centimeter of surface 15.

Preferably, layer 14 is free of any defect having a maximum dimension of greater than about 200 microns, more preferably layer 14 is free of any defect having a maximum dimension of greater than about 100 microns, and most preferably layer 14 is free of any defect having a maximum dimension of greater than about 50 microns.

Superconductor layer 14 preferably will have a critical current density of at least about $1x10^6$ Amperes per square centimeter, more preferably at least about $1.5x10^6$ Amperes per square centimeter, and most preferably at least about $2x10^6$ Amperes per square centimeter as determined by transport measurement at 77K and self field (i.e., no applied field) using a one microVolt per centimeter criterion.

Fig. 2 shows an embodiment of an article 20 that can be formed by the methods of the invention. Article 20 includes layers 12 and 14. Article 20 also includes a layer 16 disposed between layers 12 and 14 such that layer 16 is disposed on surface 13 and layer 14 is disposed on a surface 17 of layer 16.

Layer 16 can be formed of any material capable of supporting layer 14. For example, layer 16 can be formed of a buffer layer material. Examples of buffer layer materials include metals and metal oxides, such as silver, nickel, TbO_x, GaO_x, CeO_2, yttria-stabilized zirconia (YSZ), Y_2O_3, $LaAlO_3$, $SrTiO_3$, $LaNiO_3$, Gd_2O_3, $LaCuO_3$, $SrRuO_3$, $NdGaO_3$, $NdAlO_3$ and nitrides as known in the art. A buffer material can be prepared using solution phase techniques, including metalorganic deposition, such as disclosed in, for example, S.S. Shoup et al., J. Am. Cer. Soc., vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D.J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M.W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527.

In certain embodiments, an epitaxial buffer layer can be formed using a low vacuum vapor deposition process (e.g., a process performed at a pressure of at least about $1x10^{-3}$ Torr). The process can include forming the epitaxial layer using a relatively high velocity and/or focused gas beam of buffer layer material.

The buffer layer material in the gas beam can have a velocity of greater than about one meter per second (e.g., greater than about 10 meters per second or greater than about 100 meters per second). At least about 50% of the buffer layer material in the beam can be incident on the target surface (e.g., at least about 75% of the buffer layer material in the beam can be incident on the target surface, or at least about 90% of the buffer layer material in the beam can be incident on the target surface).

The method can include placing a target surface (e.g., a substrate surface or a buffer layer surface) in a low vacuum environment, and heating the target surface to a temperature which is greater than the threshold temperature for forming an epitaxial layer of the desired material on the target surface in a high vacuum environment (e.g., less than about $1x10^{-3}$ Torr, such as less than about $1x10^{-4}$ Torr) under otherwise identical conditions. A gas beam containing the buffer layer material and optionally an inert carrier gas is directed at the target surface at a velocity of at least about one meter per second. A conditioning gas is provided in the low vacuum environment. The conditioning gas can be contained in the gas beam, or the conditioning gas can be introduced into the low vacuum environment in a different manner (e.g., leaked into the environment). The conditioning gas can react with species (e.g., contaminants) present at the target surface to remove the species, which can promote the nucleation of the epitaxial buffer layer.

The epitaxial buffer layer can be grown on a target surface using a low vacuum (e.g., at least about $1x10^{-3}$ Torr, at least about 0.1 Torr, or at least about 1 Torr) at a surface temperature below the temperature used to grow the epitaxial layer using physical vapor deposition at a high vacuum (e.g., at most about $1x10^{-4}$ Torr). The temperature of the target surface can be, for example, from about 25°C to about 800°C (e.g., from about 500°C to about 800°C, or from about 500°C to about 650°C).

The epitaxial layer can be grown at a relatively fast rate, such as, for example, at least about 50 Angstroms per second.

In alternate embodiments, an epitaxial buffer layer can be deposited by sputtering from a metal or metal oxide target at a high throughput. Heating of the substrate can be accomplished by resistive heating or bias and electric potential to obtain an epitaxial morphology. A deposition dwell may be used to form an oxide epitaxial film from a metal or metal oxide target.

The oxide layer typically present on substrates can be removed by exposure of the substrate surface to energetic ions within a reducing environment, also known as Ion Beam etching. Ion Beam etching can be used to clean the substrate prior to film deposition, by removing residual oxide or impurities from the substrate, and producing an essentially oxide-free preferably biaxially textured substrate surface. This improves the contact between the substrate and subsequently deposited material. Energetic ions can be produced by various ion guns, for example, which accelerate ions such as Ar^+ toward a substrate surface. Preferably, gridded ion sources with beam voltages greater than 150 ev are utilized. Alternatively, a plasma can be established in a region near the substrate surface. Within this region, ions chemically interact with a substrate surface to remove material from that surface, including metal oxides, to produce substantially oxide-free metal surface.

Another method to remove oxide layers from a substrate is to electrically bias the substrate. If the substrate tape or wire is made negative with respect to the anode potential, it will be subjected to a steady bombardment by ions from the gas prior to the deposition (if the target is shuttered) or during the entire film deposition. This ion bombardment can clean the wire or tape surface of absorbed gases that might otherwise be incorporated in the film and also heat the substrate to elevated deposition

temperatures. Such ion bombardment can be further advantageous by improving the density or smoothness of the epitaxial film.

Upon formation of an appropriately textured, substantially oxide-free substrate surface, deposition of a buffer layer can begin. One or more buffer layers, each including a single metal or oxide layer, can be used. In some preferred embodiments, the substrate is allowed to pass through an apparatus adapted to carry out steps of the deposition method of these embodiments. For example, if the substrate is in the form of a wire or tape, the substrate can be passed linearly from a payout reel to a take-up reel, and steps can be performed on the substrate as it passes between the reels.

According to some embodiments, substrate materials are heated to elevated temperatures which are less than about 90% of the melting point of the substrate material but greater than the threshold temperature for forming an epitaxial layer of the desired material on the substrate material in a vacuum environment at the predetermined deposition rate. In order to form the appropriate buffer layer crystal structure and buffer layer smoothness, high substrate temperatures are generally preferred. Typical lower limit temperatures for the growth of oxide layers on metal are approximately 200°C to 800°C, preferably 500°C to 800°C, and more preferably, 650°C to 800°C. Various well-known methods such as radiative heating, convection heating, and conduction heating are suitable for short (2 cm to 10 cm) lengths of substrate, but for longer (1m to 100 m) lengths, these techniques may not be well suited. Also to obtain desired high throughput rates in a manufacturing process, the substrate wire or tape must be moving or transferring between deposition stations during the process. According to particular embodiments, the substrates are heated by resistive heating, that is, by passing a current through the metal substrate, which is easily scaleable to long length manufacturing processes. This approach works well while instantaneously

allowing for rapid travel between these zones. Temperature control can be accomplished by using optical pyrometers and closed loop feedback systems to control the power supplied to the substrate being heated. Current can be supplied to the substrate by electrodes which contact the substrate in at least two different segments of the substrate. For example, if the substrate, in the form of a tape or wire, is passed between reels, the reels themselves could act as electrodes. Alternatively, if guides are employed to transfer the substrate between reels, the guides could act as electrodes. The electrodes could also be completely independent of any guides or reels as well. In some preferred embodiments, current is applied to the tape between current wheels.

In order that the deposition is carried out on tape that is at the appropriate temperature, the metal or oxide material that is deposited onto the tape is desirably deposited in a region between the current wheels. Because the current wheels can be efficient heat sinks and can thus cool the tape in regions proximate to the wheels, material is desirably not deposited in regions proximate to the wheels. In the case of sputtering, the charged material deposited onto the tape is desirably not influenced by other charged surfaces or materials proximate to the sputter flux path. For this reason, the sputter chamber is preferably configured to place components and surfaces which could influence or deflect the sputter flux, including chamber walls, and other deposition elements, in locations distant from the deposition zone so that they do not alter the desired linear flux path and deposition of metal or metal oxide in regions of the tape at the proper deposition temperature.

In certain embodiments, layers 14 and/or 16 can be conditioned (e.g., thermally conditioned and/or chemically conditioned) so that surfaces 15 and/or 17 can be biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[011] or (100)[011]), has peaks in an X-ray diffraction pole figure that have a full width at half maximum of

less than about 20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°), is smoother than before conditioning as determined by high resolution scanning electron microscopy or atomic force microscopy, has a relatively high density, has a relatively low density of impurities, exhibit enhanced adhesion to other material layers (e.g., a superconductor layer or a buffer layer) and/or exhibits a relatively small rocking curve width as measured by x-ray diffraction.

"Chemical conditioning" as used herein refers to a process which uses one or more chemical species (e.g., gas phase chemical species and/or solution phase chemical species) to affect changes in the surface of a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties.

"Thermal conditioning" as used herein refers to a process which uses elevated temperature, with or without chemical conditioning, to affect changes in the surface of a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties. Thermal conditioning can be performed with or without the use of chemical conditioning. Preferably, thermal conditioning occurs in a controlled environment (e.g., controlled gas pressure, controlled gas environment and/or controlled temperature).

Thermal conditioning can include heating the surface of the layer 16 to a temperature at least about 5°C above the deposition temperature or the crystallization temperature of the underlying layer (e.g., from about 15°C to about 500°C above the deposition temperature or the crystallization temperature of the underlying layer, from about 75°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer, or from about 150°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer).

Examples of such temperatures are from about 500°C to about 1200°C (e.g., from about 800°C to about 1050°C). Thermal conditioning can be performed under a variety of pressure conditions, such as above atmospheric pressure, below atmospheric pressure, or at atmospheric pressure. Thermal conditioning can also be performed using a variety of gas environments, such as a chemical conditioning environment (e.g., an oxidizing gas environment, a reducing gas environment) or an inert gas environment.

"Deposition temperature" as used herein refers to the temperature at which the layer being conditioned was deposited.

"Crystallization temperature" as used herein refers to the temperature at which a layer of material (e.g., the underlying layer) takes on a crystalline form.

Chemical conditioning can include vacuum techniques (e.g., reactive ion etching, plasma etching and/or etching with fluorine compounds, such as BF_3 and/or CF_4). Chemical conditioning techniques are disclosed, for example, in Silicon Processing for the VLSI Era, Vol. 1, eds. S. Wolf and R.N. Tanber, pp. 539-574, Lattice Press, Sunset Park, CA, 1986.

Alternatively or additionally, chemical conditioning can involve solution phase techniques, such as disclosed in Metallurgy and Metallurgical Engineering Series, 3d ed., George L. Kehl, McGraw-Hill, 1949. Such techniques can include contacting the surface of the underlying layer with a relatively mild acid solution (e.g., an acid solution containing less about 10 percent acid, less than about two percent acid, or less than about one percent acid). Examples of mild acid solutions include perchloric acid, nitric acid, hydrofluoric acid, hydrochloric acid, acetic acid and buffered acid solutions. In one embodiment, the mild acid solution is about one percent aqueous nitric acid. In certain embodiments, bromide-containing and/or bromine-containing compositions

(e.g., a liquid bromine solution) can be used to condition the surface of a buffer layer or a superconductor layer.

Alternatively, layer 16 can be formed of a layer of superconductor material, such as an oxide superconductor material. Examples of such materials include REBCO, such as YBCO (e.g., $YBa_2Cu_3O_{7-x}$). In these embodiments, layer 16 can be prepared using the above described methods.

In certain embodiments, where layer 16 is formed of a superconductor material, layer 14 can be from solid-state, or semi solid state, precursor materials deposited in the form of a dispersion. These precursor compositions allow for example the substantial elimination of $BaCO_3$ formation in final YBCO superconducting layers, while also allowing control of film nucleation and growth.

Two general approaches are presented for the formulation of precursor compositions. In one approach, the cationic constituents of the precursor composition are provided in components taking on a solid form, either as elements, or preferably, compounded with other elements. The precursor composition is provided in the form of ultrafine particles which are dispersed so that they can be coated onto and adhere onto the surface of a suitable substrate, intermediate-coated substrate, or buffer-coated substrate. These ultrafine particles can be created by aerosol spray, by evaporation or by similar techniques which can be controlled to provide the chemical compositions and sizes desired. The ultrafine particles are less than about 500 nm, preferably less than about 250 nm, more preferably less than about 100 nm and even more preferably less than about 50 nm. In general, the particles are less than about 50% the thickness of the desired final film thickness, preferably less than about 30% most preferably less than about 10% of the thickness of the desired final film thickness. For example, the precursor composition can comprise ultrafine particles of one or more of the

constituents of the superconducting layer in a substantially stoichiometric mixture, present in a carrier. This carrier comprises a solvent, a plasticizer, a binder, a dispersant, or a similar system known in the art, to form a dispersion of such particles. Each ultrafine particle can contain a substantially compositionally uniform, homogeneous mixture of such constituents. For example, each particle can contain BaF_2, and rare-earth oxide, and copper oxide or rare earth/barium/copper oxyfluoride in a substantially stoichiometric mixture. Analysis of such particles would desirably reveal a rare-earth:barium:copper ratio as substantially 1:2:3 in stoichiometry, with a fluorine:barium ratio of substantially 2:1 in stoichiometry. These particles can be either crystalline, or amorphous in form.

In a second approach, the precursor components can be prepared from elemental sources, or from a substantially stoichiometric compound comprising the desired constituents. For example, evaporation of a solid comprising a substantially stoichiometric compound of desired REBCO constituents (for example, $YBa_2Cu_3O_{7-x}$) or a number of solids, each containing a particular constituent of the desired final superconducting layer (for example, Y_2O_3, BaF_2, CuO) could be used to produce the ultrafine particles for production of the precursor compositions. Alternatively, spray drying or aerosolization of a metalorganic solution comprising a substantially stoichiometric mixture of desired REBCO constituents could be used to produce the ultrafine particles used in the precursor compositions. Alternatively, one or more of the cationic constituents can be provided in the precursor composition as a metalorganic salt or metalorganic compound, and can be present in solution. The metalorganic solution can act as a solvent, or carrier, for the other solid-state elements or compounds. According to this embodiment, dispersants and/or binders can be substantially eliminated from the precursor composition. For example, the precursor composition

can comprise ultrafine particles of rare-earth oxide and copper oxide in substantially a 1:3 stoichiometric ratio, along with a solublized barium-containing salt, for example, barium-trifluoroacetate dissolved in an organic solvent, such as methanol.

If the superconducting layer is of the REBCO type, the precursor composition can contain a rare earth element, barium, and copper in the form of their oxides; halides such as fluorides, chlorides, bromides and iodides; carboxylates and alcoholates, for example, acetates, including trihaloacetates such as trifluroracetates, formates, oxalates, lactates, oxyfluorides, propylates, citrates, and acetylacetonates, and, chlorates and nitrates. The precursor composition can include any combination of such elements (rare earth element, barium, and copper) in their various forms, which can convert to an intermediate containing a barium halide, plus rare earth oxyfluoride and copper(oxyfluoride) without a separate decomposition step or with a decomposition step that is substantially shorter than that which may be required for precursors in which all constituents are solubilized, and without substantial formation of $BaCO_3$, and which can subsequently be treated using high temperature reaction processes to yield an epitaxial REBCO film with T_c of no less than about 89K, and J_c greater than about 500,000 A/cm^2 at a film thickness of 1 micron or greater. For example, for a $YBa_2Cu_3O_{7-x}$ superconducting layer, the precursor composition could contain barium halide (for example, barium fluoride), yttrium oxide (for example, Y_2O_3), and copper oxide; or yttrium oxide, barium trifluoroacetate in a trifluoroacetate/methanol solution, and a mixture of copper oxide and copper trifluoroacetate in trifluoroacetate/methanol. Alternatively, the precursor composition could contain Ba-trifluoroacetate, Y_2O_3, and CuO. Alternatively, the precursor composition could contain barium trifluoroacetate and yttrium trifluoroacetate in methanol, and CuO. Alternatively, the precursor composition could contain BaF_2 and yttrium acetate and CuO. In some preferred

embodiments, barium-containing particles are present as BaF_2 particles, or barium fluoroacetate. In some embodiments the precursor could be substantially a solublized metalorganic salt containing some or all of the cation constituents, provided at least a portion of one of the compounds containing cation constituents present in solid form. In certain embodiments, the precursor in a dispersion includes a binder and/or a dispersant and/or solvent(s).

The precursor compositions can be applied to substrate or buffer-treated substrates by a number of methods, which are designed to produce coatings of substantially homogeneous thickness. For example, the precursor compositions can be applied using spin coating, slot coating, gravure coating, dip coating, tape casting, or spraying. The substrate is desirably uniformly coated to yield a superconducting film of from about 1 to 10 microns, preferably from about 1 to 5 microns, more preferably from about 2 to 4 microns.

While the foregoing discussion has described multi-layer articles having two layers of material (i.e., no intermediate layer) and three layers of material (i.e., one intermediate layer), the invention is not limited in this sense. Instead, multiple intermediate layers can be used. Each of the intermediate layers can be formed of a buffer layer material or a superconductor material. For example, Fig. 3 shows a multi-layer superconductor article 30 according to yet another embodiment of the invention. Article 30 includes layers 12, 14 and 16. Article 30 further includes an additional intermediate layers 18 and 22 having surfaces 19 and 23, respectively. Layers 18 and 22 are disposed between layers 16 and 14. Each of layers 16, 18 and 22 can be formed of a buffer layer material or a superconductor material.

Superconductor articles according to the invention can also include a layer of a cap material which can be formed of a metal or alloy whose reaction products with the

superconductor material (e.g., $YBa_2Cu_3O_{7-x}$) are thermodynamically unstable under the reaction conditions used to form the layer of cap material. Exemplary cap materials include silver, gold, palladium and platinum.

In addition, while the foregoing discussion has described multi-layer articles having certain structures, the invention is not limited in this sense. For example, In some embodiments, multi-layer high temperature superconductors are provided, including first and second high temperature superconductor coated elements. Each element includes a substrate, at least one buffer layer deposited on the substrate, a high temperature superconductor layer, and optionally a cap layer. The first and second high temperature superconductor coated elements can be joined at the first and second cap layers, or can be joined with an intervening, preferably metallic, layer. Exemplary joining techniques include soldering and diffusion bonding.

Such a multi-layer architecture provides improved current sharing, lower hysteretic losses under alternating current conditions, enhanced electrical and thermal stability, and improved mechanical properties. Useful conductors can be made having multiple tapes stacked relative to one another and/or laminated to provide sufficient ampacity, dimensional stability, and mechanical strength. Such embodiments also provide a means for splicing coated tape segments and for termination of coated tape stackups or conductor elements.

Moreover, it is expected that this architecture can provide significant benefits for alternating current applications. AC losses are shown to be inversely proportional to the effective critical current density within the conductor, more specifically, the cross-sectional area within which the current is carried. For a multifilimentary conductor, this would be the area of the "bundle" of superconducting filaments, excluding any sheath material around that bundle. For a "face-to-face" architecture, the

"bundle" critical current density would encompass only the high temperature superconductor films and the thickness of the cap layer structure. The cap layer can be formed of one or more layers, and preferably includes at least one noble metal layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, the cap layer can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals). In direct current applications, additional face-to-face wires would be bundled or stacked to provide for the required ampacity and geometry for a given application.

Additionally, the high temperature superconductor film on the surface of the tapes could be treated to produce local breaks, that is, non-superconducting regions or stripes in the film only along the length of the tape (in the current flow direction). The cap layer deposited on the high temperature superconductor film would then serve to bridge the nonsuperconducting zones with a ductile normal metal region. An offset in the edge justification of the narrow strips or filaments, similar to a running bond brick pattern, would allow current to transfer to several narrow superconducting filaments both across the cap layers and to adjacent filaments, further increasing the redundancy and improving stability.

In all embodiments, a normal metal layer could be included along the edge of the conductor to hermetically seal the high temperature superconductor films and to provide for current transfer into the film, and if necessary, from the film into the substrate.

In some embodiments, coated conductors can be fabricated in a way that minimizes losses incurred in alternating current applications. The conductors are fabricated with multiple conducting paths, each of which comprises path segments which extend across at least two conducting layers, and further extend between these layers.

Each superconducting layer has a plurality of conductive path segments extending across the width of the layer, from one edge to another, and the path segments also have a component of direction along the length of the superconducting layer. The path segments in the superconducting layer surface are in electrically conductive communication with interlayer connections, which serve to allow current to flow from one superconducting layer to another. Paths, which are made up of path segments, are periodically designed, so that current flow generally alternates between two superconducting layers in bilayered embodiments, and traverses the layers through interlayer connections.

Superconducting layers can be constructed to contain a plurality of path segments which extend both across their widths and along their lengths. For example, superconducting layers can be patterned so as to achieve a high resistivity or a fully insulating barrier between each of the plurality of path segments. For example, a regular periodic array of diagonal path segments can be imposed on the layer along the full length of the tape. Patterning of superconducting layers to give such arrays can be accomplished by a variety of means known to those skilled in the art, including for example, laser scribing, mechanical cutting, implantation, localized chemical treatment through a mask, and other known methods. Further, the superconducting layers are adapted to allow the conductive path segments in their surfaces to electrically communicate with conducting interlayer connections passing between the layers, at or

near their edges. The interlayer connections will typically be normally conducting (not superconducting) but in special configurations could also be superconducting. Interlayer connections provide electrical communication between superconducting layers which are separated by non-conducting or highly resistive material which is positioned between the superconducting layers. Such non-conducting or highly resistive material can be deposited on one superconducting layer. Passages can be fabricated at the edges of the insulating material to allow the introduction of interlayer connections, followed by deposition of a further superconducting layer. One can achieve a transposed configuration with coated conductors by patterning a superconducting layer into filaments parallel to the axis of the tape and winding the tape in a helical fashion around a cylindrical form.

The following examples are illustrative only. In these examples, magnetron sputtering was conducted using a magnetron sputtering power density of from about 25 Watts per square inch to about 50 Watts per square inch and a chamber pressure of from about 10 milliTorr to about 25 milliTorr.

Example I

A precursor solution was prepared as follows. About 2.14 grams of $Y(CF_3CO_2)_3$, about 3.64 grams of $Ba(CF_3CO_2)_2$ and about 4.30 grams of $Cu(CF_3CO_2)_3$ were dissolved in about five milliliters of methanol. About 2.16 grams of water were added to the solution, and the solution volume was then adjusted to about 10 milliliters with methanol.

Example II

A buffered substrate was prepared as follows. An about 20 nanometer thick layer of CeO_2 was sputter deposited on a YSZ[100] single crystal surface at a rate of about 0.35 Angstroms per second at a temperature of about 725°C.

Example III

A multi-layer article was prepared as follows. A precursor solution prepared as described in Example I was spin coated onto a buffered substrate prepared as described in Example II.

The spin coating protocol was as follows. The buffered CeO_2/YSZ substrate was ramped from about zero revolutions per minute (RPM) to about 3000 RPM in about 0.5 second. The spin speed was held at about 3000 RPM for about five seconds and then ramped to about 5000 RPM in about 0.5 second. The spin speed was held at about 5000 RPM for about 60 seconds then reduced to about zero RPM.

The coated sample was decomposed as follows. The sample was heated from room temperature to about 220°C at a rate of about 5°C per minute in a nominal gas environment having a total gas pressure of about 760 Torr (water vapor pressure of about 32 Torr and balance oxygen). Heating was conducted in an about 2.25" diameter furnace using a gas flow rate of about 4.5 standard cubic feet per hour. The sample was held at substantially the same temperature and in substantially the same nominal gas environment for about two hours.

While keeping the sample temperature substantially constant, the gas environment was changed to 760 Torr (water vapor pressure of about 5 milliTorr and balance oxygen). The sample was held at substantially the same temperature and in substantially the same nominal gas environment for about two hours.

While keeping substantially the same nominal gas environment, the temperature was increased to about 400°C at a rate of about 5°C per minute to form an intermediate layer. The temperature was reduced to about room temperature in substantially the same nominal gas environment.

The intermediate layer was substantially defect free.

Example IV

A multi-layer article was prepared as follows. A precursor solution prepared as described in Example I was spin coated onto a buffered substrate prepared as described in Example II.

The spin coating protocol was as follows. The buffered CeO_2/YSZ substrate was ramped from about zero revolutions per minute (RPM) to about 1000 RPM in about 0.5 second. The spin speed was held at about 1000 RPM for about five seconds and then ramped to about 2000 RPM in about 0.5 second. The spin speed was held at about 2000 RPM for about 60 seconds then reduced to about zero RPM.

The coated sample was decomposed as follows. The sample was heated from room temperature to about 220°C at a rate of about 5°C per minute in a nominal gas environment having a total gas pressure of about 760 Torr (water vapor pressure of about 32 Torr and balance oxygen). Heating was conducted in an about 2.25" diameter furnace using a gas flow rate of about 4.5 standard cubic feet per hour. The sample was held at substantially the same temperature and in substantially the same nominal gas environment was for about four hours.

While keeping the sample temperature substantially constant, the gas environment was changed to 760 Torr (water vapor pressure of about 5 milliTorr and balance oxygen). The sample was held at substantially the same temperature and in substantially the same nominal gas environment for about two hours.

While keeping substantially the same nominal gas environment, the temperature was increased to about 400°C at a rate of about 5°C per minute to form an intermediate layer. The temperature was reduced to about room temperature in substantially the same nominal gas environment.

The intermediate layer was substantially defect free.

Example V

A multi-layer article was prepared as follows. A precursor solution prepared as described in Example I was spin coated onto a buffered substrate prepared as described in Example II.

The spin coating protocol was as follows. The buffered CeO_2/YSZ substrate was ramped from about zero revolutions per minute (RPM) to about 500 RPM in about 0.5 second. The spin speed was held at about 500 RPM for about five seconds and then ramped to about 1000 RPM in about 0.5 second. The spin speed was held at about 1000 RPM for about 60 seconds then reduced to about zero RPM.

The coated sample was decomposed as follows. The sample was heated from room temperature to about 220°C at a rate of about 5°C per minute in a nominal gas environment having a total gas pressure of about 760 Torr (water vapor pressure of about 32 Torr and balance oxygen). Heating was conducted in an about 2.25" diameter furnace using a gas flow rate of about 4.5 standard cubic feet per hour. The sample was held at substantially the same temperature and in substantially the same nominal gas environment for about six hours.

While keeping the sample temperature substantially constant, the gas environment was changed to 760 Torr (water vapor pressure of about 5 milliTorr and balance oxygen). The sample was held at substantially the same temperature and in substantially the same nominal gas environment for about two hours.

While keeping substantially the same nominal gas environment, the temperature was increased to about 400°C at a rate of about 5°C per minute to form an intermediate layer. The temperature was reduced to about room temperature in substantially the same nominal gas environment.

The intermediate layer was substantially defect free.

While the foregoing discussion has described the invention with respect to certain embodiments of superconductor articles and methods of making such articles, the invention is not limited in this sense. For example, the invention can relate to semiconductor articles and methods of making semiconductor articles or multi-layer articles that are electroceramics which include one or more ferroelectric layers.

Other embodiments are in the claims.

WHAT IS CLAIMED IS:

1. A method, comprising:

treating a solution using less than three temperature ramps to form a metal oxyfluoride intermediate of a rare earth metal-second metal-first metal-oxide superconductor. 2. The method of claim 1, wherein two temperature ramps are used.

3. The method of claim 1, wherein the first metal comprises copper and the second metal is selected from the group consisting of barium, strontium and calcium.

4. The method of claim 1, wherein the first metal comprises copper, and the second metal is selected from the group consisting of barium, strontium and calcium.

5. The method of claim 1, wherein the first metal comprises copper, the second metal comprises barium and the rare earth metal comprises yttrium.

6. The method of claim 1, wherein the rare earth metal-second metal-first metal-oxide comprises yttrium-barium-copper-oxide.

7. The method of claim 1, further comprising, prior to treating the solution, disposing the solution on a surface of a first layer of material.

8. The method of claim 7, wherein:

the intermediate has a surface adjacent the surface of the first layer of material,

the intermediate has a plurality of volume elements,

defects contained within the intermediate comprise less than about 20 percent of any volume element of the intermediate defined by a projection of one square centimeter of the surface of the intermediate, and

the intermediate is free of any defect having a maximum dimension of greater than about 200 microns.

9. The method of claim 1, wherein the intermediate has a thickness of at least about 0.5 micron.

10. The method of claim 1, wherein treating the solution includes heating to a first temperature of from about 215°C to about 225°C and maintaining the first temperature for at least about one hour in a first gas environment having a first water vapor pressure.

11. The method of claim 10, wherein the first temperature is about 220°C.

12. The method of claim 10, wherein the first water vapor pressure is from about 17 Torr to about 40 Torr.

13. The method of claim 10, further comprising maintaining the first temperature for at least about one hour in a second gas environment having a second water vapor pressure different than the first water vapor pressure.

14. The method of claim 13, wherein the second water vapor pressure is less than the first water vapor pressure.

15. The method of claim 13, wherein the second water vapor pressure is less than about one Torr.

16. The method of claim 13, further comprising heating to a second temperature different than the first temperature and maintaining the second temperature for a time period sufficient to form the metal oxyfluoride intermediate.

17. The method of claim 16, wherein the second temperature is about 400°C.

18. The method of claim 16, wherein heating to the second temperature is performed in the second gas environment.

19. The method of claim 16, further comprising heating to a third temperature to form the rare earth-second metal-first metal-oxide superconductor, the third temperature being different than the second temperature.

20. The method of claim 19, wherein the third temperature is at least about 700°C.

21. A method, comprising:

heating a solution to a first temperature and maintaining the first temperature for a first time period, the first temperature being greater than room temperature and the first period of time being at least about one minute; and

heating to a second temperature greater than the first temperature to form a metal oxyfluoride intermediate of a rare earth-second metal-first metal-oxide superconductor.

22. The method of claim 21, wherein the first time period is at least about five minutes.

23. The method of claim 21, wherein the first time period is at least about 30 minutes.

24. The method of claim 21, wherein the first time period is at least about one hour.

25. The method of claim 21, wherein the first time period is at least about two hours.

26. The method of claim 21, wherein the first time period is at least about four hours.

27. The method of claim 21, wherein the first temperature is at least about 50°C.

28. The method of claim 21, wherein the first temperature is at least about 100°C.

29. The method of claim 21, wherein the first temperature is at least about 150°C.

30. The method of claim 21, wherein the first temperature is at least about 200°C.

31. The method of claim 21, wherein the first temperature is from about 215°C to about 225°C.

32. The method of claim 21, wherein the first metal comprises copper and the second metal is selected from the group consisting of barium, strontium and calcium.

33. The method of claim 21, wherein the first metal comprises copper, and the second metal is selected from the group consisting of barium, strontium and calcium.

34. The method of claim 21, wherein the first metal comprises copper, the second metal comprises barium and the rare earth metal comprises yttrium.

35. The method of claim 21, wherein the rare earth metal-second metal-first metal-oxide comprises yttrium-barium-copper-oxide.

36. The method of claim 21, further comprising, prior to treating the solution, disposing the solution on a surface of a first layer of material.

37. The method of claim 36, wherein:

the intermediate has a surface adjacent the surface of the first layer of material,

the intermediate has a plurality of volume elements,

defects contained within the intermediate comprise less than about 20 percent of any volume element of the intermediate defined by a projection of one square centimeter of the surface of the intermediate, and

the intermediate is free of any defect having a maximum dimension of greater than about 200 microns.

38. The method of claim 21, wherein the intermediate has a thickness of at least about 0.5 micron.

39. The method of claim 21, wherein the second temperature is about 400°C.

40. The method of claim 21, further comprising heating the metal oxyfluoride intermediate to a third temperature to form the rare earth-second metal-first metal-oxide superconductor, the third temperature being different than the second temperature.

41. The method of claim 40, wherein the third temperature is at least about 700°C.

42. A method, comprising:

heating a solution to a first temperature;

maintaining the first temperature for a first time period of time in a first gas environment having a first water vapor pressure, the first temperature being greater than room temperature and the first period of time being at least about one minute;

maintaining the first temperature for a second period of time in a second gas environment having a second water vapor pressure different than the first water vapor pressure, the second time period being at least about one minute; and

heating to a second temperature greater than the first temperature to form a metal oxyfluoride intermediate of a rare earth-second metal-first metal-oxide superconductor.

43. The method of claim 42, wherein the first water vapor pressure is greater than the second water vapor pressure.

44. The method of claim 42, wherein the first water vapor pressure is from about 17 Torr to about 40 Torr.

45. The method of claim 42, wherein the first water vapor pressure is about 32 Torr.

46. The method of claim 42, wherein the second water vapor pressure is less than about one Torr.

47. The method of claim 42, wherein the second water vapor pressure is less than about 0.1 Torr.

48. The method of claim 42, wherein the second water vapor pressure is less than about 10 milliTorr.

49. The method of claim 42, wherein the second water vapor pressure is about 5 milliTorr.

50. The method of claim 42, wherein the first time period is at least about one hour.

51. The method of claim 42, wherein the second time period is at least about one hour.

52. The method of claim 42, wherein the first metal comprises copper and the second metal is selected from the group consisting of barium, strontium and calcium.

53. The method of claim 42, wherein the first metal comprises copper, and the second metal is selected from the group consisting of barium, strontium and calcium.

54. The method of claim 42, wherein the first metal comprises copper, the second metal comprises barium and the rare earth metal comprises yttrium.

55. The method of claim 42, wherein the rare earth metal-second metal-first metal-oxide comprises yttrium-barium-copper-oxide.

56. The method of claim 42, further comprising, prior to treating the solution, disposing the solution on a surface of a first layer of material.

57. The method of claim 46, wherein:

the intermediate has a surface adjacent the surface of the first layer of material,

the intermediate has a plurality of volume elements,

defects contained within the intermediate comprise less than about 20 percent of any volume element of the intermediate defined by a projection of one square centimeter of the surface of the intermediate, and

the intermediate is free of any defect having a maximum dimension of greater than about 200 microns.

58. The method of claim 42, wherein the intermediate has a thickness of at least about 0.5 micron.

59. The method of claim 42, wherein the second temperature is about 400°C.

60. The method of claim 42, further comprising heating the metal oxyfluoride intermediate to a third temperature to form the rare earth-second metal-first metal-oxide superconductor, the third temperature being different than the second temperature.

61. The method of claim 60, wherein the third temperature is at least about 700°C.

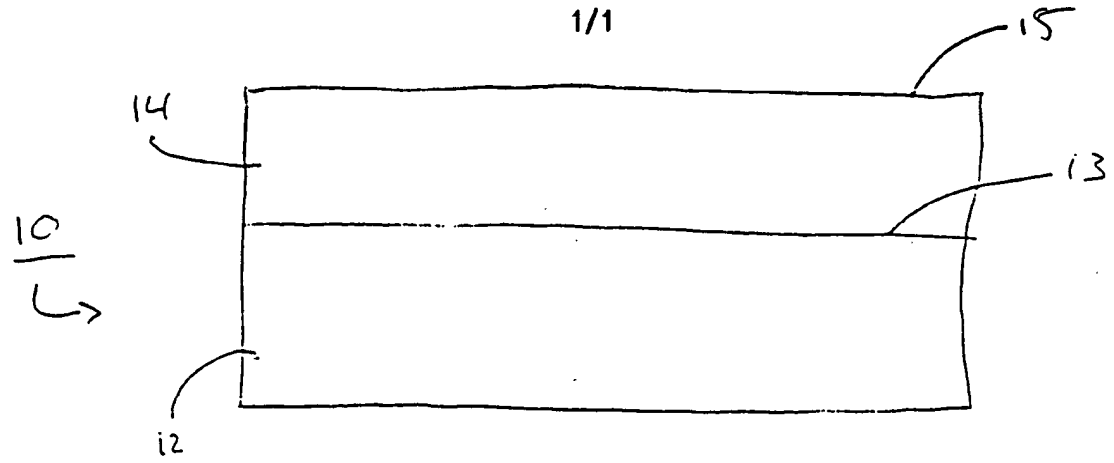


Fig. 1

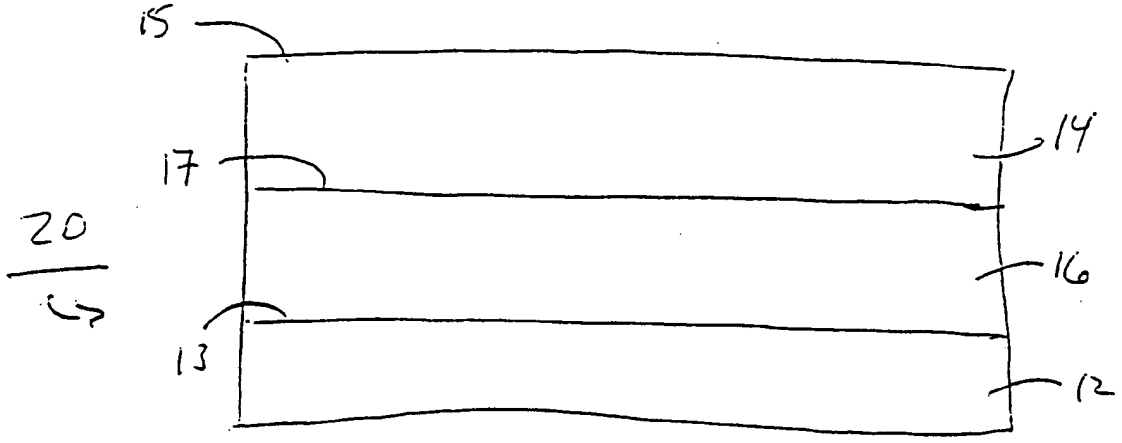


Fig. 2

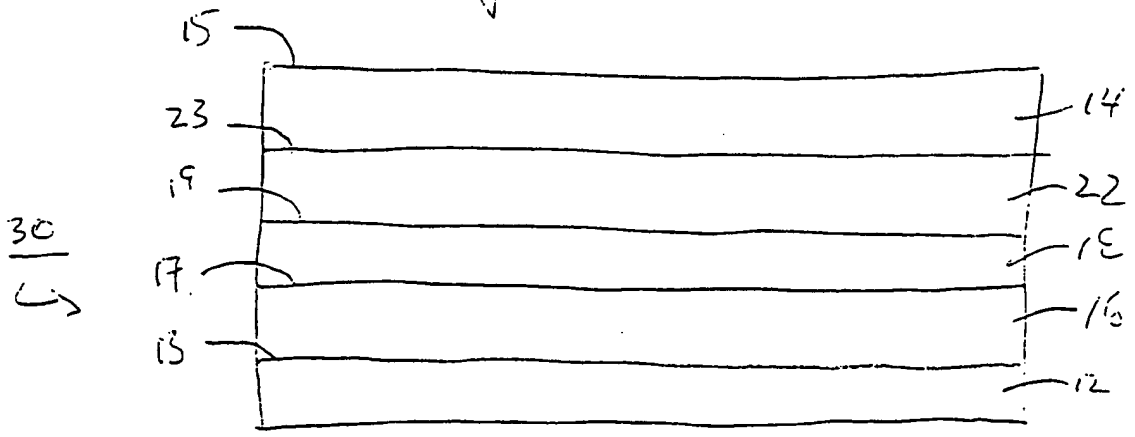


Fig. 3